

RESERVE

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements relating to the Polymerisation of Vinyl Compounds

We, THE PERMUTIT COMPANY LIMITED, a British Company, of Permutit House, Gunnersbury Avenue, London, W.4, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that vinyl compounds can be polymerised by dispersing the monomer through a second phase, generally water, and subjecting the mixture to the influence of heat in the presence of a catalyst, which is generally dissolved in the monomer. The monomer is agitated during the polymerisation and forms globules which polymerise to solid spheres. As the polymerisation proceeds the globules become increasingly viscous and as they collide with one another under the influence of agitation they tend to coalesce. This can be prevented by introducing into the system a stabilising substance which forms a protective coating round the globules. Various substances, both organic and inorganic and including various phosphates, have been proposed as stabilisers. It has been found that so much stabiliser has been necessary as to make it difficult to remove the stabiliser from the finished polymer beads. It is therefore desirable to find improved stabilisers.

According to this invention one or more basic pyrophosphates of calcium, magnesium, zinc, cobalt, nickel, mercury (mercuric), manganese, copper (cupric), aluminium and iron (ferric) is or are used as a stabiliser. These basic pyrophosphates contain a proportion of metal in excess of the amount in the corresponding simple pyrophosphates. For instance, calcium pyrophosphate has the formula $\text{Ca}_2\text{P}_2\text{O}_7$, whereas the basic calcium pyrophosphate has the approximate composi-

tion $3\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{Ca}(\text{OH})_2$, the molar ratio of $\text{CaO} : \text{P}_2\text{O}_5$ being 2.7:1. In general the compositions of the various basic pyrophosphates differ according to the particular metal, but the molar ratio of metal oxide; P_2O_5 is always less than 3.0:1. For the bivalent metals the ratio is between 2.7:1 and 3.0:1 while for the trivalent metals aluminium and iron the ratio is between 0.8:1 and 1.0:1.

During the polymerisation reaction acidic oxidation products may be formed and tend to decompose the basic pyrophosphate. In any case, it is essential that the pH of the mixture is at or above 7, and accordingly adjustment of the pH must be made if necessary. In general, the pH should not exceed 10.

The basic pyrophosphates named above are insoluble in water and tend to collect at the surface of the monomer globules, thus forming a sort of cushion, so that when two globules collide under the influence of the stirring they do not coalesce as two plain droplets would do, but bounce apart and still retain their spherical form. Although almost all the heavy metal pyrophosphates are insoluble in water it is only those named which give a satisfactory stabilising effect. Others are so dense that even under the influence of stirring they tend to fall to the bottom of the vessel, an example of this being barium pyrophosphate, while yet others fail for no apparent reason at all.

The basic pyrophosphate may be prepared in solution and then filtered off and added, with or without drying, to the suspension polymerisation system, but it is much preferred to form the stabiliser *in situ* in the vessel in which the polymerisation is to take place.

The basic pyrophosphate may be prepared by mixing an aqueous solution of a

soluble normal pyrophosphate and a soluble salt of the appropriate metal. An excess of the metal salt is required over that necessary to form the normal pyrophosphate, and under these conditions the hydroxides of certain metals, namely aluminium, zinc, iron, cobalt, nickel, mercury, manganese and copper may also be precipitated with the basic pyrophosphate. To minimise this it is desirable to add no more than a 50% molar excess of the soluble salt of the metal over the amount required to make the normal pyrophosphate. About 35% excess is required to form the basic pyrophosphate itself, so that the excess in this case should be no more than 15%. The soluble pyrophosphate solution used in making the basic pyrophosphate should not be heated and, if the metal salt solution has been heated to hasten dissolution of the salt, it should be cooled before mixing with the pyrophosphate solution. This is to prevent the formation of orthophosphate, which may occur at elevated temperatures.

The process of this invention enables a high ratio of monomer to water to be used in the polymerisation system with very small quantities of the stabilizer. Thus monomer-water ratios as high as 1:1 can be used with an amount of stabiliser equal to 0.1% by weight of the system, all the monomer being recovered as discrete and regular spheres of polymer.

These stabilisers can be used for the suspension polymerisation of various vinyl monomers, for example, styrene and methyl methacrylate, or mixtures of monomers, for example, styrene and divinyl benzene, styrene and ethylene dimethacrylate, methyl methacrylate and divinyl benzene, vinyl acetate and divinyl benzene.

Some examples will now be given.

EXAMPLE 1

2.4 grams of anhydrous sodium pyrophosphate were dissolved at room temperature in 380 cc. of water while stirring mechanically. 2.8 grams of anhydrous calcium chloride were dissolved in 20 cc. of water and added to the stirred pyrophosphate solution. The pH of the mixture was then adjusted to 10 with dilute ammonia solution. A mixture of 200 cc. of styrene and 14 cc. of divinyl benzene concentrate (containing 50% divinyl benzene) in which was dissolved 1.0 gram of benzoyl peroxide, was added to the mixture whereupon the liquid mixture of monomers broke up into globules of approximately 1 mm. diameter. The whole was heated on a water bath to 75–80° C. and the stirring and

heating were continued until hard spheres of the polymer were formed. 180 grams of perfect spheres of a styrene-divinyl-benzene copolymer were obtained.

EXAMPLE 2

A solution of 6.0 gms. of hydrated manganese chloride in 50 cc. of water was added to a stirred solution of 2.6 gms. of anhydrous sodium pyrophosphate in 350 cc. of water. Sufficient dilute ammonia solution was added to bring the pH to 9. To this suspension was added a mixture of 7 cc. of ethylene diamethacrylate and 200 cc. of styrene in which 1.0 gm. of benzoyl peroxide was dissolved. The mixture was shaken cautiously until the droplets were of the required size and then stirred slowly. The temperature was raised to 75–80° C. and the heating continued until hard spheres of the polymer were formed.

EXAMPLE 3

3.5 gm. of hydrated cobalt chloride were dissolved in 50 cc. of water. This solution was added to a solution of 1.3 gm. anhydrous sodium pyrophosphate in 150 cc. of water. The pH was adjusted to 7.5 with dilute sodium hydroxide solution. To this suspension was added a mixture of 2 cc. of divinyl benzene concentrate (containing 50% divinyl benzene) and 98 cc. of styrene in which 0.5 gm. of benzoyl peroxide had been dissolved. The mixture was warmed to 75–80° C. while stirring mechanically to produce droplets of the desired size. The temperature was kept in this range until hard beads were formed. These were washed free of stabiliser with hot water and then kept in boiling water for two hours to complete the polymerization. The product was all in the form of hard spheres of between 0.27 and 1.08 mm. diameter.

What we claim is:—

1. A process for the suspension polymerisation of a vinyl compound in which one or more basic pyrophosphates of calcium, manganese, zinc, cobalt, nickel, mercury (mercuric), manganese, copper (cupric), aluminium and iron (ferric) is or are used as a stabiliser and the pH is maintained at or above 7 during the polymerisation.

2. A process according to claim 1 in which the stabiliser is formed *in situ* in the vessel in which the polymerisation takes place.

3. A process according to claim 2 in which the basic pyrophosphate is prepared by mixing an aqueous solution of a soluble normal pyrophosphate and a soluble salt of the appropriate metal in an amount in excess of that necessary to form the normal pyrophosphate.

4. A process according to claim 1 substantially as described with reference to any of the examples herein.

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PROVISIONAL SPECIFICATION

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We, THE PERMUTIT COMPANY LIMITED, a British Company, of Permutit House, Gunnersbury Avenue, London, W.4, do hereby declare this invention to be described in the following statement:—

It is known that vinyl compounds can be polymerised by dispersing the monomer throughout a second phase, generally water, and subjecting the mixture to the influence of heat in the presence of a catalyst, which is generally dissolved in the monomer. The monomer is agitated during the polymerisation and forms globules which polymerise to solid spheres. As the polymerisation proceeds the globules become increasingly viscous and as they collide with one another under the influence of agitation they tend to coalesce. This can be prevented by introducing into the system a stabilising substance which forms a protective coating round the globules. Various substances, both organic and inorganic, have been proposed as stabilisers. It has been found that relatively large quantities of stabiliser have been necessary; this makes it difficult to remove the stabiliser from the finished polymer beads. It is therefore desirable that as small a quantity of stabiliser as possible should be used.

According to this invention one or more basic pyrophosphates of calcium, magnesium, zinc, cobalt, nickel, mercury (mercuric, manganese, copper (cupric), aluminium and iron (ferric) is or are used as a stabiliser. These basic pyrophosphates contain a proportion of metal in excess of the amount in the corresponding simple pyrophosphates. For instance, calcium pyrophosphate has the formula $\text{Ca}_2\text{P}_2\text{O}_7$, whereas the basic calcium pyrophosphate has the approximate composition $3\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{Ca}(\text{OH})_2$, the molar ratio of $\text{CaO}:\text{P}_2\text{O}_5$ being 2.7:1. In general the compositions of the various metal pyrophosphates differ according to the particular metal, but the molar ratio of metal oxide: P_2O_5 is always less than 3.0:1. For the bivalent metals the ratio is between 2.7:1 and 3.0:1 while for the trivalent metals aluminium and iron the ratio is between 0.8:1 and 1.0:1.

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influence of the stirring they do not coalesce as two plain droplets would do, but bounce apart and still retain their spherical form. Although almost all the heavy metal pyrophosphates are insoluble in water it is only those named which give a satisfactory stabilising effect. Others are so dense that even under the influence of stirring they tend to fall to the bottom of the vessel, an example of this being barium pyrophosphate while yet others fail for no apparent reason at all.

The basic pyrophosphate may be prepared in solution and then filtered off and added, with or without drying, to the suspension polymerisation system, but it is much preferred to form the stabiliser *in situ* in the vessel in which the polymerisation is to take place. The basic pyrophosphate will form only at a pH between 7 and 10, and accordingly adjustment of the pH to bring it into this range must be made if necessary.

The basic pyrophosphate may be prepared by mixing an aqueous solution of a soluble normal pyrophosphate and a soluble salt of the appropriate metal. An excess of the metal salt is required over that necessary to form the normal pyrophosphate, and under these conditions the hydroxides of certain metals, namely aluminium, zinc, iron, cobalt, nickel, mercury, manganese and copper may also be precipitated with the basic pyrophosphate. To minimise this it is desirable to add no more than a 50% molar excess of the soluble salt of the metal over the amount required to make the normal pyrophosphate. About 35% excess is required to form the basic pyrophosphate itself, so that the excess in this case should be no more than 15%. The soluble pyrophosphate solution used in making the basic pyrophosphate should not be heated and, if the metal salt solution has been heated to hasten dissolution of the salt, it should be cooled before mixing with the pyrophosphate solution. This is to prevent the formation of orthophosphate, which may occur at elevated temperatures.

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be used with an amount of stabiliser equal to 0.1% by weight of the system, all the monomer being recovered as discrete and regular spheres of polymer.

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An example will now be given.

- 15 2.4 grams of anhydrous sodium pyrophosphate were dissolved at room temperature in 380 cc. of water while stirring mechanically. 2.8 grams of anhydrous calcium chloride were dissolved in 20 cc. of water and added to the

stirred pyrophosphate solution. The pH of the mixture was then adjusted to 10 with dilute ammonia solution. A mixture of 200 cc. of styrene and 14 cc. of divinyl benzene concentrate (containing 25 50% divinyl benzene) in which was dissolved 1.0 gram of benzoyl peroxide, was added to the mixture whereupon the liquid mixture of monomers broke up into globules of approximately 1 mm. diameter. The whole was heated on a water bath to 75–80° C. and the stirring and heating were continued until hard spheres of the polymer were formed. 180 grams of perfect spheres of a styrene-divinyl- 30 benzene copolymer were obtained.

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